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A Comparison of Composite Transparent Conducting Oxides Based on the Binary Compounds CdO and SnO₂

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Introduction

Transparent conducting oxides (TCOs) are used extensively for a variety of applications including architectural windows, flat-panel displays, thin-film photovoltaics, smart windows, and polymer-based electronics. Some of these applications constitute a very large market, indicating that TCOs are of great commercial importance. The work on TCO semiconductors such as tin oxide (SnO₂), cadmium oxide (CdO), and cadmium stannate (Cd₂SnO₄) has been of great technological interest due to their high quality of electrical and optical properties. Owing to their durability, conductive SnO₂ films on glass substrates are used extensively for low-E glass windows for energy conservation and thin-film photovoltaic solar cells. CdO thin film (polycrystalline) is not a popular TCO material due to its narrow optical bandgap. However, it has demonstrated unusually high electron mobility that is 5-10 times higher than commercially available TCOs. Thin films of Cd₂SnO₄ combine the characteristics of SnO₂ and CdO and are known to have high electron mobility, high electrical conductivity, and low visible absorption, which makes them suitable for a wide range of applications. Cd₂SnO₄ is an n-type semiconductor with either orthorhombic or spinel crystal structures.

Chemical-vapor deposition (CVD) is a thin-film formation technique that is easy to scale up and is widely used by industry. In this report, we will first discuss the properties of CVD-formed SnO₂ and CdO thin films and their composite Cd_ySn_xO_{2x+y}. We will then compare the electronic and optical properties of Cd_ySn_xO_{2x+y} to those of SnO₂ and CdO.

CVD-Formed SnO₂ Thin Films

Commercially available SnO₂ thin films typically are deposited by atmospheric pressure, chemical-vapor deposition (APCVD) using tetrachloride (TTC). Researchers have demonstrated those higher-quality film results when TTC is replaced with tetramethyltin (TMT). However, due to the greater toxicity and cost of TMT compared to TTC, relatively few detailed studies have been performed on the properties of TMT-produced films. We treat the issue of toxicity very carefully. The deposition system used for this study is in a vented enclosure that is maintained at a negative pressure to minimize any impact due to accidental leakage. To ensure that toxic materials are not exhausted during operation, an effluent treatment system using a pyrolyzer and water scrubber is incorporated into the system.

We have studied the intrinsic and fluorine-doped SnO₂ films using low-pressure, chemical-vapor deposition (LPCVD) with TMT, oxygen, and bromotrifluoromethane (CBrF₃) as precursor. The TMT chemistry, combined with the LPCVD process, produces film properties that are easily controlled and reproduced. The SnO₂ films formed with TMT also demonstrate higher transparency and higher conductivity compared to that commercially available films produced using TTC.

The temperature window for SnO₂ film growth is between 500° and 700°C. The film structure and the morphology are affected slightly with growth temperature. X-ray diffraction (XRD) analysis reveals that the film is well crystallized at 500°C. Intrinsic SnO₂ films are randomly oriented, whereas F-doped films exhibit a strong (200) preferred orientation. As growth temperature increases, atomic force microscopy and transmission electron microscopy analyses show that the crystallization and grain size increase. Thus, the intensity of the XRD spectrum and the surface roughness increase.

SnO₂ with a tetragonal structure is naturally a weak n-type semiconductor due to a deviation from stoichiometry. Further n-type doping can be achieved using antimony, chlorine, and fluorine (F). We investigated F-doped SnO₂ films. Due to the high volatility of the CBrF₃ precursor, the F-doping efficiency is strongly dependent on the substrate temperature and reaction chamber pressure. Secondary-ion mass spectrometry (SIMS) analysis has revealed that the F-doping level depends logarithmically on the CBrF₃ partial pressure and the electronic concentration depends logarithmically on the F-doping level. Hall measurements show that without F-doping, the film resistivity is ~1 Ω-cm. With F-doping, the film resistivity is ~5x10⁻⁴ Ω-cm. F doping not only increases the carrier concentration, but also increases the electron mobility (μ) of the film. This observation is contrary to what is expected from ionized impurity scattering. For undoped SnO₂ films, the μ is ~1 cm²V⁻¹s⁻¹ and electron concentration is in the low-10¹⁸ cm⁻³ range. Assuming oxygen vacancies (V_O²⁻) are dominant donors in undoped SnO₂, and each V_O²⁻ contributes two electrons to SnO₂, for a carrier concentration of low 10¹⁸ cm⁻³, the V_O²⁻ concentration should be about high-10¹⁷ cm⁻³. For F-doped SnO₂ films, the electron concentration increases to mid-10²⁰ cm⁻³, which indicates the F⁺ ion concentration should also be mid-10²⁰ cm⁻³. Although the ion concentration increases significantly for F doping, the μ does not decrease, but increases from ~1 cm²V⁻¹s⁻¹ to 40 cm²V⁻¹s⁻¹. This observation indicates that the ion

scattering is not a dominant scattering mechanism for SnO_2 :F film.

The optical properties of doped and undoped SnO_2 films were also compared. Generally, for SnO_2 films that are $\sim 1 \mu\text{m}$ thick, the average transmission is $>80\%$ in the visible spectral range. Spectrophotometric analysis also shows that F-doped films have higher absorption than the undoped films. For undoped SnO_2 films, the optical absorption (average between 500 and 900nm) is $\sim 600 \text{ cm}^{-1}$ compared to $\sim 1200 \text{ cm}^{-1}$ for F-doped film.

CVD-Formed CdO Thin Films

Among the various TCO thin films, cadmium oxide (CdO) has received perhaps the least attention. Reasons for this most likely include the toxicity of Cd and the relatively narrow bandgap of CdO. CdO is an n-type semiconductor with a bandgap of 2.28 eV, which is smaller than both SnO_2 (3.6 eV) and indium tin oxide (ITO) (3.6 eV), the two most widely used TCOs. CdO thin films have been deposited using reactive sputtering, spray pyrolysis, and activated reactive evaporation. Our group is the first to report depositing CdO thin films by MOCVD.

We found that, due to the nature of the dimethylcadmium (DMC) precursor, CdO film properties are very sensitive to the deposition temperature within the range of $100^\circ\text{--}450^\circ\text{C}$. CdO films have a cubic structure. At growth temperature below 250°C , the films are weakly crystallized, with grains randomly oriented on the glass substrate. At temperatures above 300°C , the CdO films are strongly crystallized, with a preferred (200) orientation. At deposition temperatures above 400°C , the TEM images show that CdO films have a nearly perfect intragrain structure.

Without doping, the CdO can be a very strong n-type semiconductor and its carrier concentration will be very sensitive to temperature. At a substrate temperature of 100°C , the film carrier concentration reaches $1.9 \times 10^{21} \text{ cm}^{-3}$. As temperature increases, the carrier concentration decreases but the electron mobility increases from ~ 1 to $220 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. With the high intragrain crystal quality we have achieved, the extremely high electronic properties of CdO thin films have been demonstrated. The Hall mobility observed on CdO films deposited at substrate temperature 450°C is substantially greater than the values reported for films formed by other techniques and even for bulk material. For example, the highest Hall mobility previously reported is $135 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for films made by

activated reactive evaporation. Values reported for spray pyrolysis and dc-reactive sputtering are $\sim 70 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively.

In the visible-wavelength range, CdO film has a lower transmission than SnO_2 . The CdO films appear light yellow due to its narrow optical bandgap. However, the small effective mass of CdO produces a large Burstein-Moss shift. Thus, as the carrier concentration increases, we have observed that the bandgap of CdO increases from 2.3 eV to 3.3 eV.

CVD-Formed CdSnO_x Thin Films

The cadmium tin oxide compound generally has two forms: CdSnO_3 and Cd_2SnO_4 . CdSnO_3 has orthorhombic and rhombohedral structures; Cd_2SnO_4 has orthorhombic and cubic spinel structures. Cd_2SnO_4 film with the spinel structure is one of the more promising new TCO compounds because of higher mobility and low visible absorption. Most Cd_2SnO_4 thin films are made by sputtering, but some are made by spray pyrolysis. To our knowledge, Cd_2SnO_4 films have not yet been made by CVD.

We have produced the $\text{Cd}_y\text{Sn}_x\text{O}_{2x+y}$ by combining our SnO_2 and CdO CVD procedures. X-ray photoemission spectroscopy analyses indicate that the compositions of $\text{Cd}_y\text{Sn}_x\text{O}_{2x+y}$ films formed in this study encompass a wide compositional range from CdO- to SnO_2 -like materials. As a result, the crystal structure of cubic (CdO-like), cubic spinel (Cd_2SnO_4 -like), and tetragonal (SnO_2 -like) structures have been observed by XRD. The carrier concentration of the films also varies with composition from mid 10^{20} cm^{-3} to a high of 10^{17} cm^{-3} . As the carrier concentration decreases, the Hall mobility increases from less than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $\sim 60 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Even the highest mobility data obtained from $\text{Cd}_y\text{Sn}_x\text{O}_{2x+y}$ is lower than those from CdO are, but higher than those from SnO_2 . Spectrophotometric analysis indicates that the optical bandgap increases from 2.75 eV (CdO-like) to 3.65 eV (SnO_2 -like) due to the changes of composition and carrier concentration. The wide variation in both optical and electronic properties may offer composite $\text{Cd}_y\text{Sn}_x\text{O}_{2x+y}$ films a wide range of applications. Also, this direct information on the CdO- Cd_2SnO_4 - SnO_2 phase formation and resultant electro-optical properties may lead to an increased understanding of both the materials systems, and provide guidance toward the fabrication of large-area, single-phase Cd_2SnO_4 by CVD.